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CHEMICAL REACTIONS AND PROPERTIES OF ORGANOSILICON
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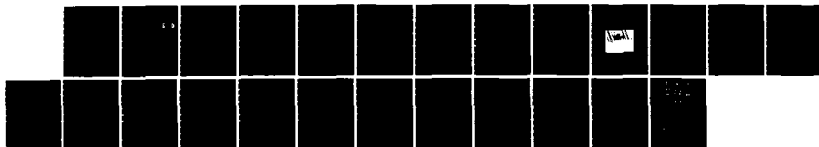
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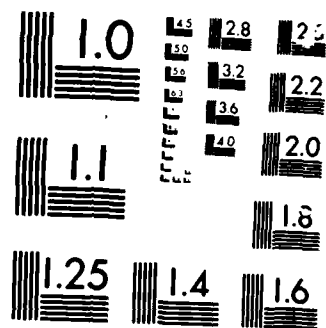
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Final Technical Report

CHEMICAL REACTIONS AND PROPERTIES OF ORGANOSILICON
COMPOUNDS RELATED TO NEW MATERIALS

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The Air Force Office of Scientific Research
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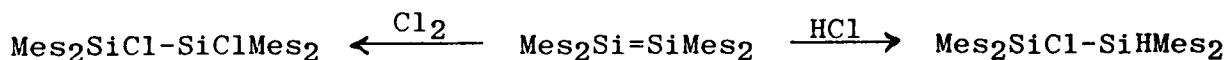
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<p>Chemistry of compounds containing silicon-silicon double bonds was investigated. Two new disilenes were synthesized and rotational barriers to <i>cis-trans</i> interconversion were determined to be 25-31 Kcal/mol. Oxidation of disilenes led to the 1,3-cyclodisiloxanes, as well as to disilene epoxide and 1,2-dioxetanes, all novel structures. Many new polysilane high polymers were synthesized, and their photoactivity was investigated. Several new methods for crosslinking of polysilanes were developed, and the first polysilanes containing functional side groups were prepared. Several cyclosilane families of compounds were also investigated.</p>					
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Part. I. Disilene Chemistry (in collaboration with Prof. J. Michl, University of Utah)

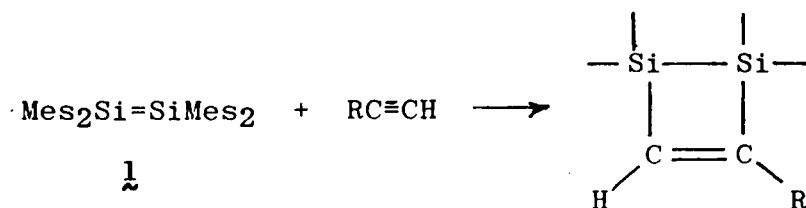
In December of 1982 our initial report was published on tetramesityldisilene, the first compound containing a silicon-silicon double bond. Considerable national and international publicity arose from this breakthrough, which seemed likely to open a large new area of silicon chemistry. The key compound is made by photolysis of a trisilane precursor at -80°C :



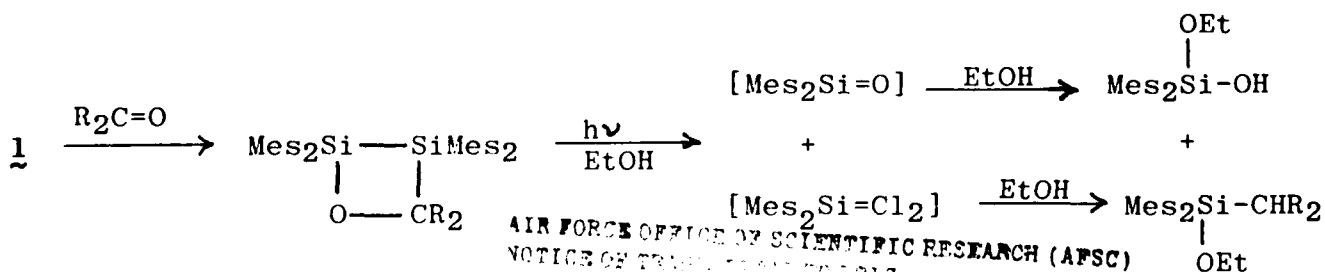
During the period covered by this report, a number of chemical reactions of tetramesityldisilene have been carried out. The compound behaves like an olefin in some reactions, for instance addition of hydrogen halides or chlorine:



It will also undergo cycloaddition with acetylenes to give the corresponding disilacyclobutenes:

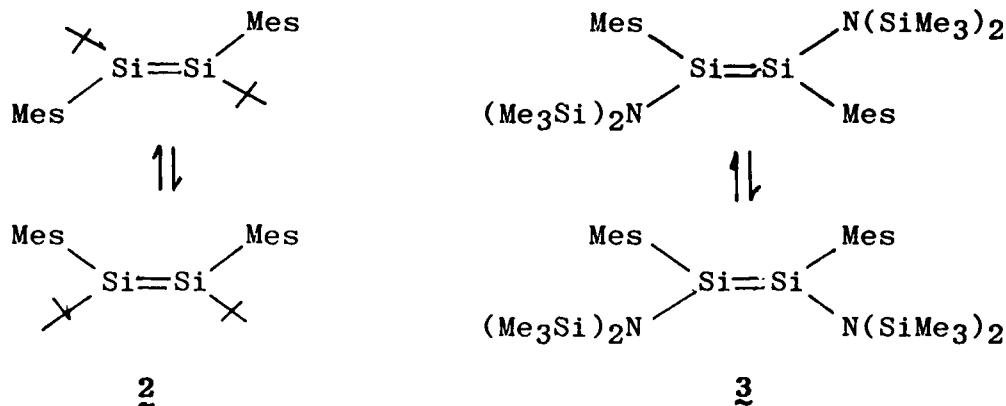


Carbonyl compounds also cycloadd to 1 to give four-membered ring compounds. Upon photolysis in the presence of ethanol, the latter are cleaved to form species containing Si=O and Si=C double bonds, which are trapped by reaction with ethanol:



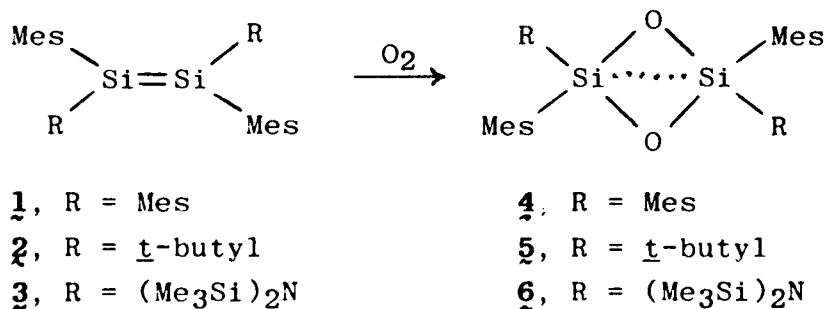
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Chief, Technical Information Division

By similar photolysis of trisilane precursors two new disilenes **2** and **3** have been prepared. Because they contain different substituents on each silicon atom, **2** and **3** can exist as cis or trans stereoisomers.

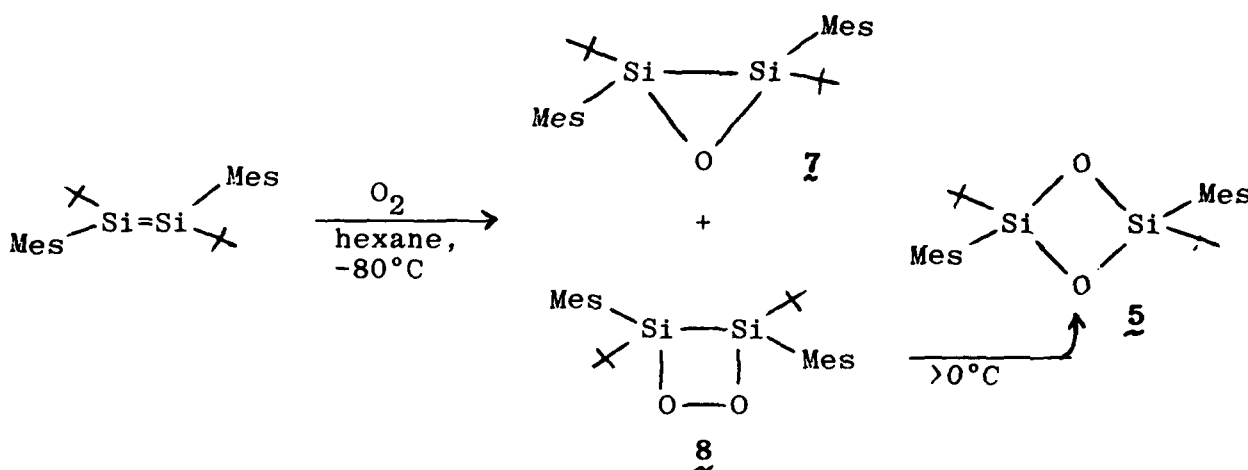


Compound **2** is initially obtained in the trans form but can be converted to a 40:60 mixture of cis and trans isomers by irradiation with ultraviolet light. Compound **3** is initially isolated as the cis isomer, but slowly transforms to the trans isomer at room temperature in solution. Studies of the rates of cis-trans interconversion of **2** and **3** show that the activation energies for this process are between 25 and 30 Kcal/mol. This is the first measurement of the "energy" of the Si-Si pi bond. The value is approximately half as large as for a normal carbon-carbon pi-bond.

The three known disilenes all react with oxygen at room temperature to give similar dioxygen adducts, with four-membered ring structures, compounds **4**, **5** and **6**. The structure of **4** has been determined by x-ray crystallography; it shows a remarkably short Si-Si distance of 231 pm (2.31Å). This is even less than the usual Si-Si distance between silicon atoms which form a single bond. In addition, the Si-O-Si bond angles are surprisingly small, 86°. These results suggest that a silicon-silicon bond is present in **4**. However if that is so, there are not enough electrons to form single Si-O bonds around the ring, and the Si-O bonds must be electron deficient. The structures of **4-6** thereby provide a new and unsolved problem in chemical bonding.

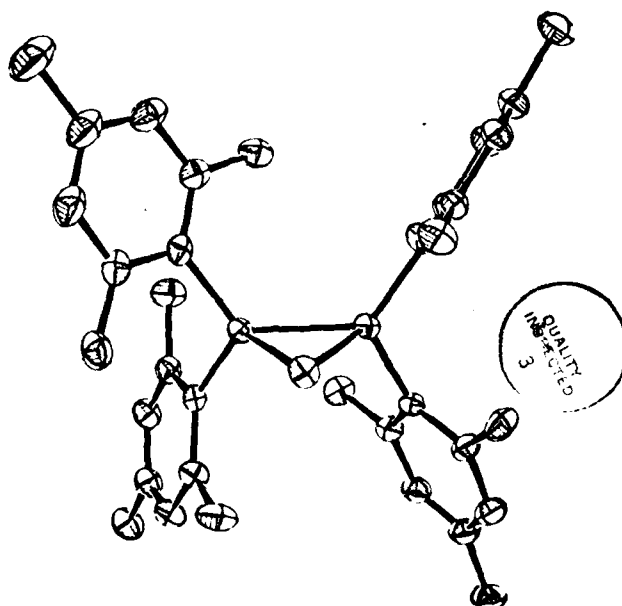


However at low temperatures in solution, oxidation of **2** produces no **5**. The products are instead the "epoxide" **7** and the 1,2-dioxetane **8**. Upon warming above 0°C, **9** slowly isomerizes to **5**; the oxidation is fully stereospecific. Both **7** and **8**



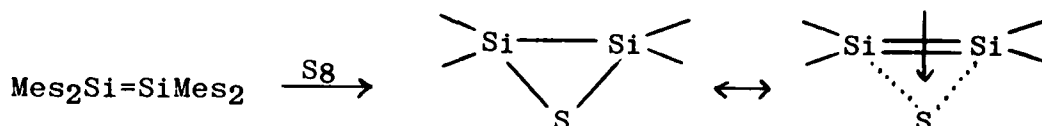
are previously unknown types of compounds. The crystal structures of these substances are under investigation.

Reaction of **1** or **2** with sulfur produces three-membered ring compounds. The structure for the product from **1**, determined by x-ray crystallography, is shown below. Remarkable



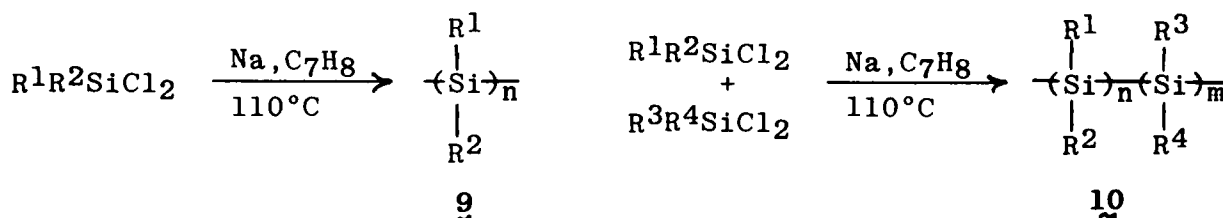
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features of the structure are a very short Si-Si bond length, indicating partial multiple bonding between the silicon atoms; and a nearly planar arrangement of the carbon and silicon atoms around each silicon. These facts suggest that the molecule may be a pi-complex between the Si-Si double bond and a sulfur atom:



Part II. Polysilane Polymers

Many examples of polysilane high polymers have been synthesized during the period covered in this report. These polymers are prepared from diorganodichlorosilanes and sodium metal; either homopolymers (9) or copolymers (10) may be made:



The polysilane polymers are meltable and soluble in organic solvents; they can be cast into films, formed into solid objects by molding, or drawn into fibers. Three important uses for polysilane polymers are under development in other laboratories: 1. As pyrolytic precursors to silicon carbide, in the form of fibers, coatings or solid matrices; 2. As photoresist materials for the manufacture of computer microchips and other micro-electronic components; and 3. As photoinitiators for polymerization of acrylates and other vinyl compounds.

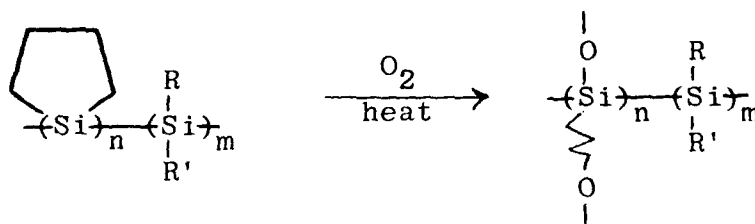
A. Crosslinkable Polysilanes

Silicon carbide is potentially very important as a part of Air Force structural materials, such as high-strength composites, turbine blades, etc. There is much interest in making silicon carbide from polymeric precursors such as polysilanes. However, in using polysilanes to generate silicon carbide, a

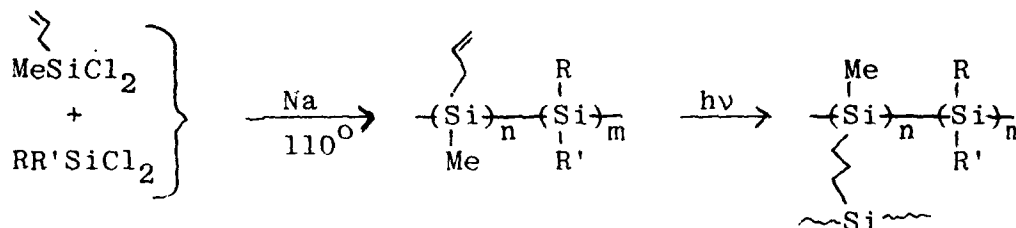
major problem has been to bring about strong crosslinking, so that the maximum amount of silicon is retained during thermolysis. Without crosslinking, much of the silicon in the polymer is lost upon heating, as volatile silanes, and the yield of silicon carbide is therefore greatly reduced.

During the grant period we have developed five new polysilane systems which can be readily crosslinked. These should be superior starting materials for the synthesis of silicon carbide by thermolysis.

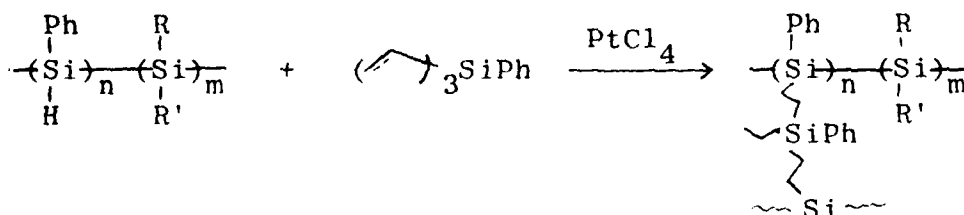
1. The first of these systems consists of copolymers which include silicon atoms in five-membered rings containing four carbon atoms. Upon exposure to oxygen above room temperature, some of these rings open with oxidation and crosslinking takes place through oxygen:



2. We have found that allyl groups can be incorporated into polysilane polymers. The resulting allylsilane copolymers undergo rapid and efficient crosslinking when they are exposed to ultra-violet light:

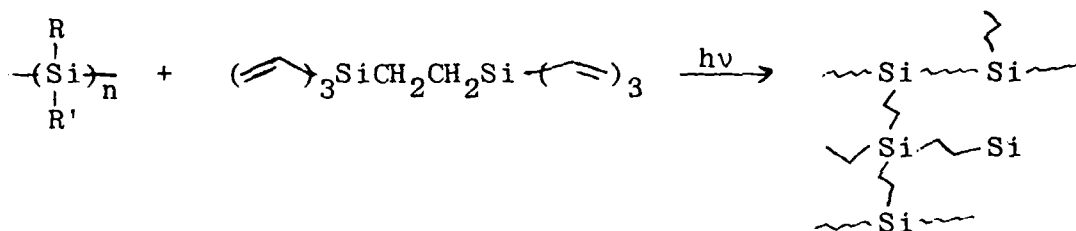


3. Using special techniques, polymers have been synthesized which contain some silicon atoms bonded to hydrogen. These become crosslinked when mixed with substances containing several vinyl groups, in the presence of a PtCl_4 catalyst. A typical vinyl compound useful in this process is trivinylphenylsilane:



This chemical crosslinking takes place at room temperature, making possible the room temperature vulcanization of polysilanes. The process is analogous to room temperature vulcanization which is used in silicone polymer technology ("RTV silicones").

4. Any polysilane polymer, mixed with a compound containing several vinyl groups, can be rapidly crosslinked with ultraviolet radiation. A typical compound used in this process is hexavinyl-disilabutane:



5. The same process as in 4. can be accomplished using a free-radical initiation such as a peroxide, and heat, in place of ultraviolet irradiation.

These processes may make possible a more efficient preparation of silicon carbide from polysilane chemical precursors.

B. Polysilanes as Photoresists for Computer Chip and Printed Circuit Manufacture

The usefulness of polysilanes as photoresist materials was a joint discovery between this group and scientists at the IBM San Jose Research Laboratories. Photoresists are a crucial part of modern electronics, upon which all of our defense effort is based. The complex topography necessary on silicon chips and integrated circuits can be generated only by photoresist technology.

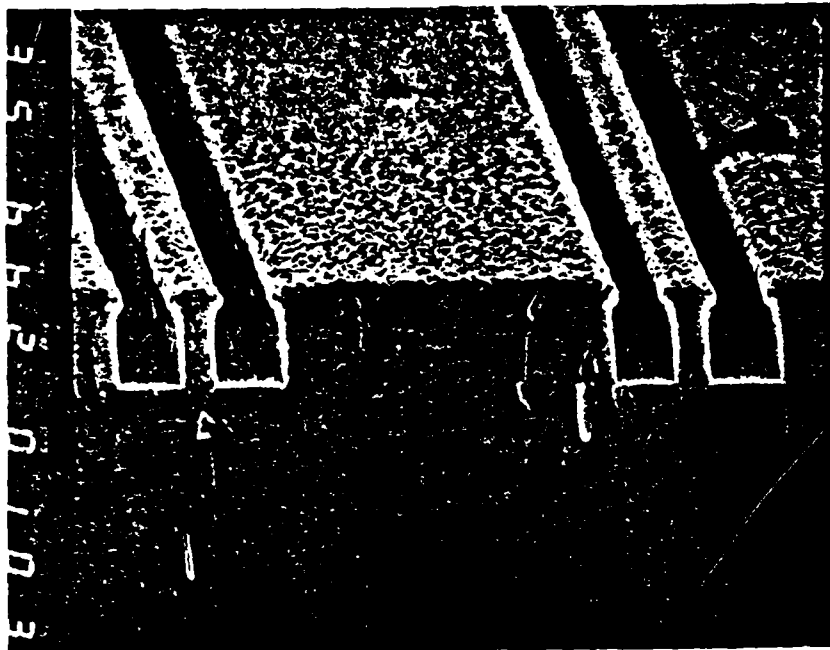
Photoresists work in two modes: positive, in which the exposed polymer is made more soluble so that it can be removed, leaving the unexposed polymer in place; and negative, in which the exposed polymer is crosslinked to make it less soluble, so that it will remain behind while the unexposed material is removed. Polysilanes, unlike any other known photoresist materials, can be made to work in either mode. At the moment the greatest interest is in polysilane positive resists.

Several physical properties of polysilanes make them especially desirable as photoresist materials: 1. Very high extinction coefficients in the ultraviolet region; 2. Rapid and efficient photoreactions (either chain scission or crosslinking); 3. The wavelength of the absorption maximum decreases with decreasing molecular weight. These properties combine to give the polysilanes exceptional sensitivity in photoresist applications. In addition

a further property is most important. Because they are silicon polymers, they can be oxidized in an oxygen plasma to convert them to a highly resistant silicon dioxide on the surface. Thus once the desired topography is generated, it can be made resistant to further chemical attack.

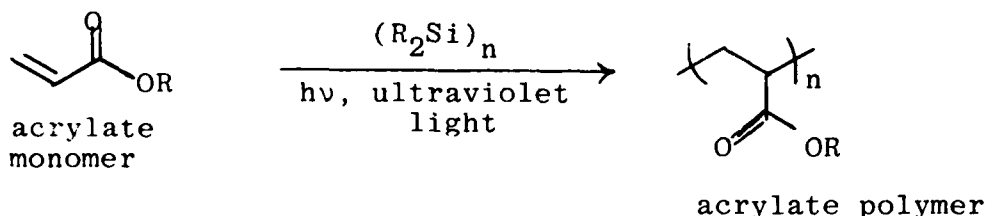
The efficiency of solid-state electronics is limited by the pattern resolution, that is by the distance between "lines" imprinted as the resist material on a computer chip. Using polysilane photoresists, resolution has been achieved which is better than the present state of the art.

A figure showing silicon chip topography generated using a polysilane photoresist is shown below. The line-to-line resolution in the photograph is $0.83\text{ }\mu\text{m}$.



C. Photopolymerization of Vinyl Monomers

A major finding during the period of this contract is that polysilane polymers are highly efficient catalysts for the ultraviolet photopolymerization of vinyl monomers to polymers and plastics. A typical application is in the polymerization of acrylates and methacrylates:



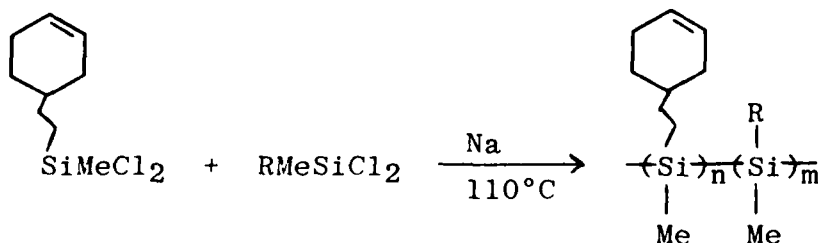
The limits of this discovery are still being investigated; styrene is also rapidly polymerized by this means, and we believe it will work with any monomer which will undergo free-radical polymerization.

The catalysis seems to be general for all polysilane polymers, regardless of their composition. The ultraviolet light can be in the range from 250 to 350 nm, depending on the absorption maximum for the polysilane. Because the polysilanes are strong absorbers of ultraviolet radiation and highly efficient catalysts, very small amounts are required in this process. Moreover, photocatalysis using polysilanes produces polymers with higher molecular weights than by other methods. This may lead to significant improvements in the properties of the resulting polymers.

This discovery may be important to the Air Force as well as to many other branches of industry. For example, photopolymerization is used in making adhesives useful in airframe manufacture; in making photoresists for the manufacture of printed circuits and computer chips; and in coatings of optical fibers used in telecommunications.

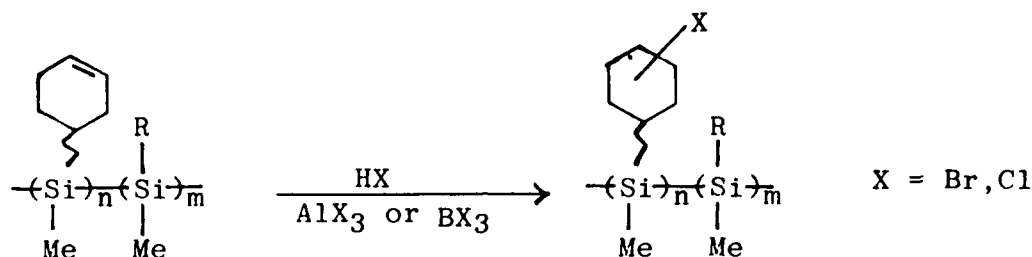
D. New Developments

A series of polymers was synthesized containing 3-cyclohexenylethyl groups:



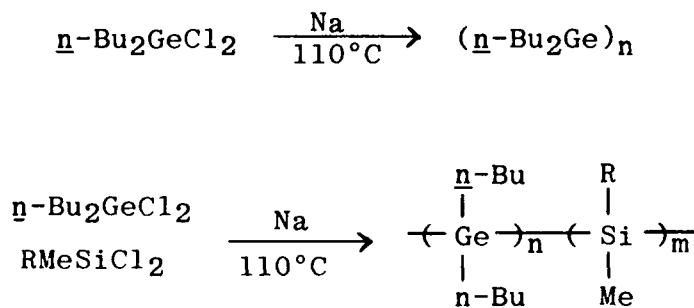
These are the first polysilane polymers containing a functional group (the carbon-carbon double bond) in the side chain. Reaction of 3-5 with HCl or HBr in the presence of Lewis acid

catalysts produced polymers containing halogen atoms in the side chain. These also are the first such polymers to be made:



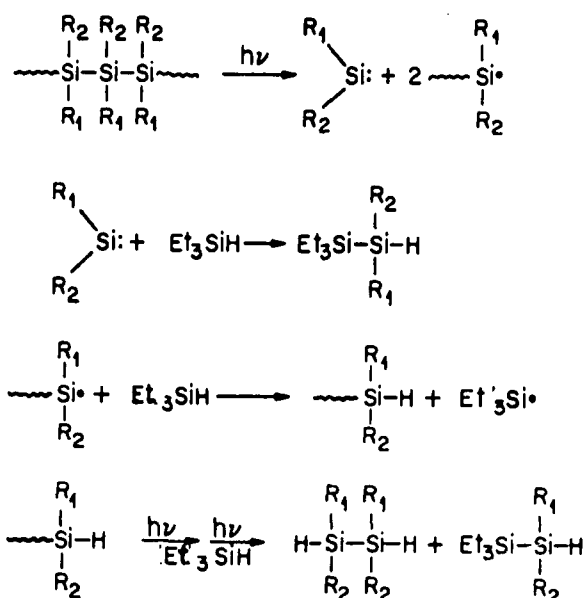
The bromine-containing polymers, because they contain a heavy atom, may be superior photoresist materials for x-ray or electron-beam photolithography. These are advanced techniques for computer-chip manufacture which are expected to become increasingly important with further miniaturization.

A polygermanium polymer, and several mixed polysilane-polygermanes, have also been synthesized:



The germanium polymer and copolymers show the same photosensitivity as the polysilanes, and slightly longer absorption wavelengths. Therefore they may also be useful as photoresist materials for microlithography in the electronics industry.

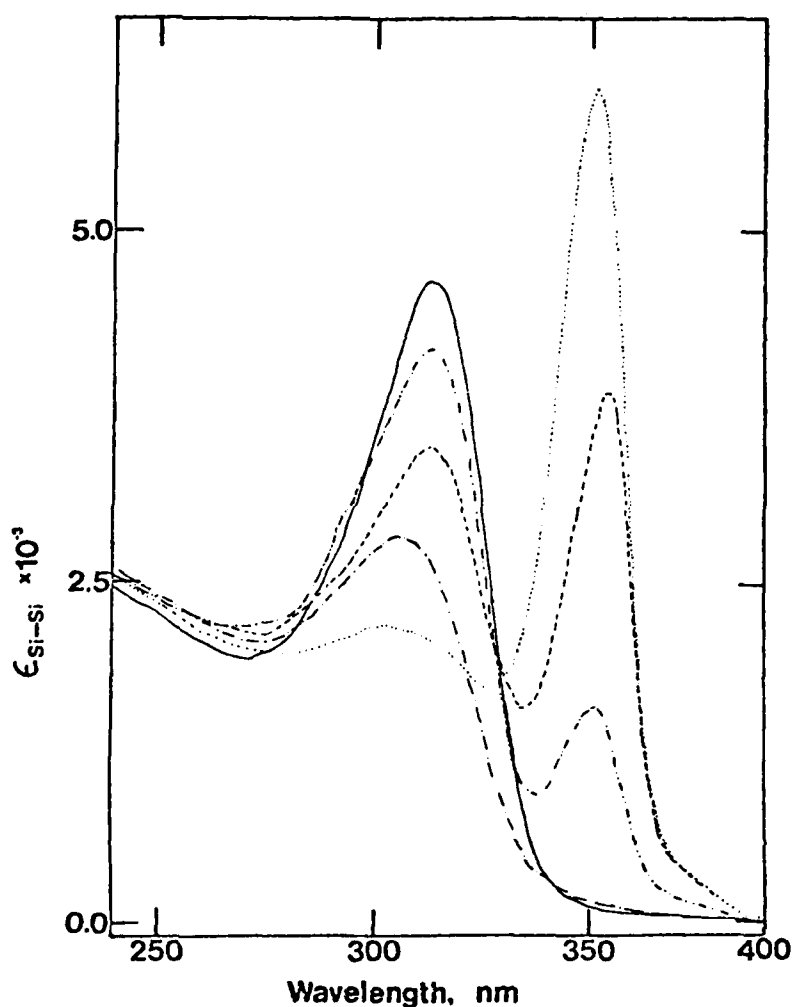
The scission of polysilane polymers under the influence of ultraviolet light has been studied by isolating the products of photodegradation. From these results, a cascade mechanism of photodegradation has been proposed, as shown below:



Mechanistic hypothesis for the photodegradation of high molecular weight polysilane derivatives.

The first experiments to investigate polysilane polymers by silicon-29 NMR spectroscopy were carried out during 1984. It seems likely that this information will be extremely important for the understanding of the detailed structure of polysilane polymers. These initial results are very promising, and this study will be continued in 1985.

An important recent discovery was the UV thermochromism of polysilane high polymers. As temperature is decreased, some polysilanes undergo a gradual shift of their absorption band to lower energy (longer wavelength). This behavior itself is surprising. However, polysilane polymers with long-chain alkyl groups on the silicon undergo a truly remarkable change as temperature is decreased; the polysilane absorption band disappears and is replaced by a new band at lower energy. The following figure illustrates this for di-*n*-butylpolysilylene. This unprecedented effect will be investigated more fully in the future.



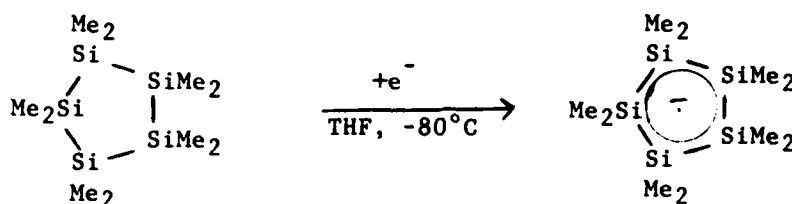
UV spectrum of a 0.0055% solution of $(n\text{-Bu}_2\text{Si})_n$ in hexane: (---), 72°C; (—), 18.5°C, (-·-·), -18.5°C; (- - -), -38°C; (···), -61°C.

Part III. Cyclic Polysilanes

The cyclic polysilanes, $(\text{RR}'\text{Si})_n$ where $n = 4$ to 35, have been studied in our laboratories for nearly 20 years. It was investigations of these cyclic molecules which led ultimately to discovery of the soluble polysilane polymers, discussed in Part II of this report. The cyclic molecules are of interest because the electrons in the silicon-silicon bonds are highly delocalized. That is, these electrons move freely from one

silicon atom to another--just as electrons do in elemental silicon in microelectronic devices such as computer chips.

Some of the best evidence for electron delocalization comes from study of the anion-radicals of these cyclic silanes by electron spin resonance spectroscopy. The anion-radicals are made by reducing the cyclosilanes either electrochemically or with alkali metals, in solvents such as tetrahydrofuran (THF). An example is the reduction of $(\text{Me}_2\text{Si})_5$ to $(\text{Me}_2\text{Si})_5^{\cdot-}$:

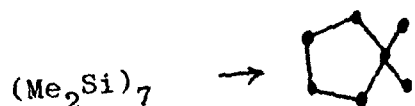


Recently, we have determined the ESR spectra for a number of new cyclosilane anion-radicals. From these spectra, the hyperfine splitting constants (hfsc) for silicon-29 and carbon-13 have been evaluated; selected data are shown in the following table.

ESR Parameters for Cyclosilane Anion-Radicals

Anion-Radical	Color	Splitting Constant, G		
		²⁹ Si	¹³ C	¹ H
$(\text{Me}_2\text{Si})_4$	blue	-	21.0	0.67
$(\text{Et}_2\text{Si})_4$	blue	4.7	18.4	<0.14
$(i\text{-Pr}_2\text{Si})_4$	olive	3.8	18.6, 14.4	<0.31
$(\text{Me}_2\text{Si})_5$	blue	5.2	16.0	0.53
$(\text{Et}_2\text{Si})_5$	blue	4.4	14.1	<0.04
$(n\text{-Pr}_2\text{Si})_5$	blue	4.0	13.4	<0.18
$(\text{Me}_2\text{Si})_6$	yellow	-	14.6	0.44

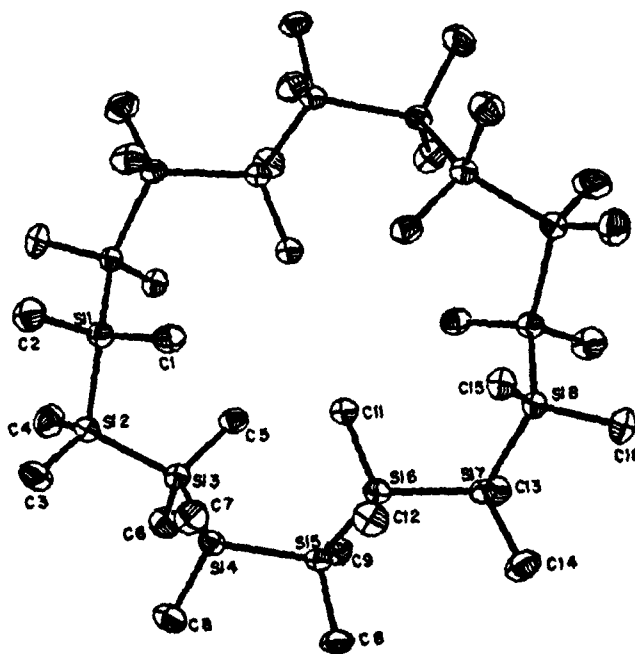
The aluminum chloride catalyzed rearrangement of permethylpolysilanes has been investigated. Typically, ring contraction reactions take place to give branched, five-membered ring products, whose nature is quite specific:



(Dots represent
silicon atoms
in the products)

The electronic properties of these products are under investigation.

X-ray crystal structure studies have been completed for the two methylcyclosilanes, $(\text{Me}_2\text{Si})_7$ and $(\text{Me}_2\text{Si})_{16}$. The structures are quite different from those found for the corresponding hydrocarbons, $(\text{CH}_2)_7$ and $(\text{CH}_2)_{16}$. A diagram of the unusual, folded structure of $(\text{Me}_2\text{Si})_{16}$ is shown below.



COMPLETED PROJECT SUMMARY

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3. **INCLUSIVE DATES:** February 1, 1982 - September 30, 1985
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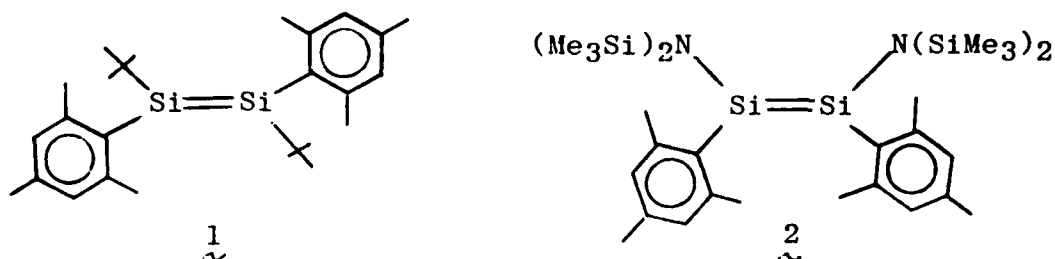
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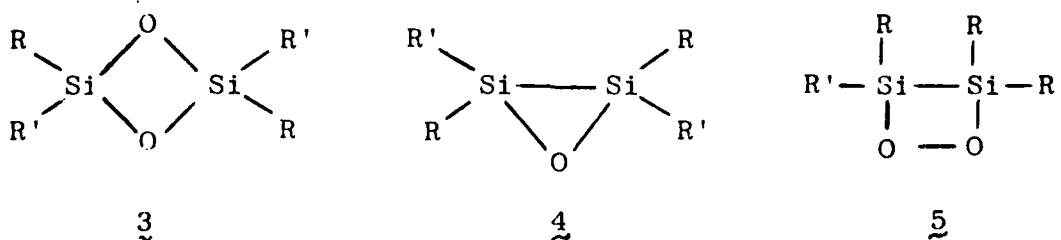
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9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

During the 44 months covered by this report, substantial work was done to explore the chemistry of the disilenes, compounds with silicon-silicon double bonds. The first disilene was isolated shortly before this report period. Two new disilenes, 1 and 2, were synthesized, and crystal structures for two of the compounds were determined. Rotational barriers for cis and trans interconversion of disilenes were investigated; for 1,2-di-tert-butyl-1,2-dimesityl disilene, 1. The barrier is ~30 Kcal/mole, providing a minimum value for the Si-Si pi bond energy.

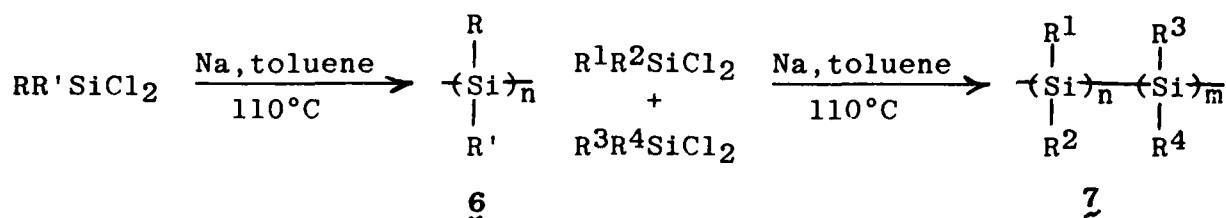


Reaction of disilenes with oxygen led to the first cyclo-disiloxanes (3). Intermediate oxidation products 4 and 5 were also prepared. The crystal structure of compound 3 shows an



extremely short Si-Si bond length of ~231 pm; these compounds therefore present a new and as yet unsolved problem in chemical bonding theory.

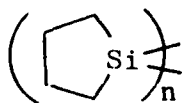
The chemistry of polysilane high polymers was greatly developed during the period covered by this report. These materials contain only silicon atoms in the polymer backbone; homopolymers (6) or copolymers (7) can be made:



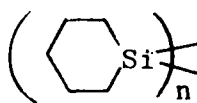
These polymers are of technological interest as 1. Precursors to high-strength silicon carbide ceramics; 2. Photoresist materials for the manufacture of improved microelectronic components, and 3. Photoinitiators for polymerization of vinyl monomers.

Many new polysilane polymers were synthesized during the time of this report. The photoactivity and the mechanism of photodegradation of the polymers, important in their use in the manufacture of silicon microchips, was investigated. Molecular mechanics calculations were used to study the conformations of polysilane chains. Several new methods for crosslinking of polysilanes were developed; this is essential in the use of these materials for making silicon carbide. The first polysilane with functional groups in the organic side chains were synthesized. Finally, the activity of the polysilanes as photoinitiators for vinyl polymerization was discovered.

Cyclic polysilanes were also investigated. The synthesis and chemical reactions of the diethyl and ethylmethylcyclosilanes, $(\text{Et}_2\text{Si})_n$ and $(\text{EtMeSi})_n$, were studied, and the first organosilicon rotanes, **8** and **9**, were isolated. A comprehensive study of the electron spin resonance spectra of cyclosilane anion-radicals led to a new model for the bonding and electron distribution in these molecules.



8, n = 5 to 15



9, n = 4-6

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